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JACOBS ENGINEERING GROUP INC.
ENVIRONMENTAL SYSTEMS DIVISION

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June 13, 1988

Mr. Gerardo Armador
Environmental Protection Agency
Region III
841 Chestnut Building
Philadelphia, Pennsylvania 19107

Re: Radon Gas Levels and Biotransformation of Compounds
Project No. 05B87700,
Work Assignment C03001
Du Pont Newport Site, Region III

Dear Gerardo:

Please find enclosed for your information:

1. Copy of Paper, Geological Factors that Influence Radon Availability. This paper was provided by Douglas Gonzales, PhD, Senior Health Physicist, Jacobs, to provide us a better understanding of Radon Gas sources.
2. Copy of Study, Potential Biotransformation of Chemical Compounds by Rajagopal Krishnamoorthy, PhD., Jacobs. This study was conducted to support a groundwater contamination assessment. Based on this study, PCE, TCE, DCE, Methylene Chloride and Chloroform found in the North Disposal Site, will degrade over a period of time. If the source is cleaned up, then the groundwater contamination will eventually disappear.

Sincerely yours,

JACOBS ENGINEERING GROUP INC.

Paul Fikac
Region VI
Work Assignment Manager

PF/mjo

Enclosures

cc: M. Warner
File

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POSTER PAPER SESSION

GEOLOGICAL FACTORS THAT INFLUENCE
RADON AVAILABILITY

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There is great need for the characterization of localities with respect to their potential for supplying radon to structures, especially where the number of existing structures is insufficient for valid sampling. Although the interaction between a structure and the ground is not quantitatively known, it is practical to assume that the ground can be characterized as to the rate at which radon can be drawn from it by a structure; a measure of radon availability. Radon availability is related mainly to the concentration of radon in the spaces in rock fractures and soil pores and to the permeability of the ground to gases. The fraction of radium disintegrations producing radon that reaches those spaces usually falls within the range of 0.15 to 0.55. Permeability and the diffusion coefficient are related markedly as the sizes of those spaces are reduced and as the proportion of the spaces filled by liquids is increased. Coupling this knowledge with that of the geology, soil, hydrology, and topography of a locality should permit qualitative evaluation of radon availability. Rock types that usually have above-average concentrations of radon in the pore and fracture spaces are granites, some gneisses, phosphatic rocks, mafic shales, and recrystallized limestones and dolomites. Construction of buildings in contact with such rocks, if fractured, is unwise. Basal soils, notably LEIS FORMS, are often enriched in radium. Ground with coarse grain size (such as gravels and coarse sands), particularly if well-drained, is highly permeable and apt to make more radon available than would be expected on the basis of its radium content. At the other extreme, muds and clays tend to be of low permeability, especially if wet. Ground that does not pass a percolation test should have low radon availability unless enriched in radium. Buildings located on hillsides and ridges are more apt to be located on soils that are coarser and better drained than those in adjacent valleys. Other things being equal, radon availability should be greater on hillsides and ridges.

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GEOLOGICAL FACTORS THAT INFLUENCE RADON AVAILABILITY

Introduction

During the period following the discovery of very high indoor radon levels in some houses near Boyertown, Pennsylvania, the U. S. Geological Survey has received many requests for information about the geologic distribution and exact locations of areas having the potential to supply enough radon to houses and other structures to bring indoor radon concentrations to a level of concern. Often it has been assumed that a map of known occurrences of radium or uranium, or of geologic formations known to be enriched in radium or uranium, would suffice to show the locations of houses likely to have elevated levels of indoor radon. The assumption is proving to be naive. This paper is a presentation of the principles relevant to the production and movement of radon in the ground, of methods of identifying areas likely to have indoor radon problems, of geologic correlations with indoor radon surveys that have been noted to date, and of speculation on the radon potential of certain rock and soil types and landforms.

Sources of Indoor Radon

Radon, radium, and uranium are present in all soils. A gross correlation between the concentration of uranium or radium in the ground and indoor radon decay product levels has been observed, but is not by itself adequate to enable us to identify specific localities as being "likely" or "unlikely". The lack of close correlation is due to the fact that indoor radon arises from a combination of three or four factors, all of which must be better known before we can make adequate predictions as to the radon levels in houses in a given area.

The three or four factors, or conditions for radon entry into structures, are: (1) there must be radium in the ground, (2) radon produced by decay of the radium must be able to move to a structure, (3) there must be pathways for entry of radon into the structure, and (4) efficient movement of radon into the structure usually requires that the atmospheric pressure in the structure be lower than it is in the soil. The first two conditions pertain to the geologic environment; the latter two are features that are unique to the building, and are the subject of the next paper in this conference. It is important to note that the latter two conditions have influenced the results of surveys of indoor radon in various countries.

Figure 1 shows a generalized probability frequency distribution called log-normal. It is characterized by having the greatest probabilities of occurrence toward a low value of the independent variable, but significant probabilities at high values. It has several different and distinct applications to indoor radon. Practically all surveys of indoor radon have yielded log-normal distributions, in which case we mark the horizontal coordinate as indoor radon, in increments of radon concentration (or working levels), and the vertical coordinate as the percentage of houses falling within each increment. I emphasize that the results of indoor radon surveys include the effects of all the conditions for radon entry, both the geologic conditions and the building characteristics.

Let us consider what would be obtained by a survey of many houses that were built on ground having the same characteristics (uniform intrinsic radon concentration in the soil and uniform in all factors that determine radon movement in the soil). We should very likely observe substantial variation in indoor radon from house to house, and it should not be a surprise if an indoor radon survey yielded a log-normal distribution. If one attempted

to characterize the radon potential of the ground on the basis of a small number of measurements, how would he know that he was taking samples near the median, rather than toward the low or high end? This is the essential problem that arises when the radon potential of a locality is to be judged by indoor radon surveys.

From the standpoint of prediction, it should be more efficient and reliable if we could first obtain an empirical relation between indoor radon concentrations and some parameter that was characteristic of conditions of the ground only, independent of a structure built on it, and then classify localities by the values of that parameter. The possibilities are discussed in a section below.

Geological Conditions for Radon Entry

Radium Distribution. The first radon entry condition has to do with the radium distribution in the ground. Usually only the top few meters of soil are important, but radium situated more deeply can be a source of fractured rock is nearby, or if the soil is very coarse sand or gravel.

In order to discuss the correlation between uranium and radium in the ground, it is necessary to be familiar with the decay of the radioactivity series that is headed by uranium-238, shown in Figure 2. One should know that four of these radionuclides, uranium-238, uranium-234, thorium-230 and radium-226, are long-lived and have such different chemical characteristics that they are frequently separated by geochemical processes. Uranium (uranium-238) is generally immobile in reducing environments and mobile in oxidizing environments. If radioactive equilibrium prevails, uranium-234 is present at a concentration lower than that of its parent uranium-238 by a factor of 18,000; its movement is much less restricted by the law of mass-action. Thorium-230 is the least mobile, probably because of adsorption on silicates. Radium (radium-226) is fairly mobile in reducing environments, although it is adsorbed on peaty material, but in oxidizing environments radium tends to be scavenged by oxidizing iron or manganese or to be coprecipitated with alkaline-earth compounds, particularly with calcium carbonate. In natural waters, uranium and its radium progeny are effectively separated, so that reconnaissance measurements of uranium in waters give little specific information about radium distribution in an area.

Since the atomic energy program began, people have devoted much labor to the search for uranium, rather than radium. Because uranium has been the valuable commodity, some geologic formations or deposits hundreds of feet underground often have been worthwhile exploration targets and have been reported and appear on maps as uranium occurrences or ore bodies. Although they may contribute radioactivity to well waters, their presence on maps can be very misleading, because they are buried too deeply to contribute radon to structures.

What is known about radium distribution? In addition to the reports by Myrick and others¹ and by Hollenberg and Smith², there is the large set of data generated by the National Uranium Resource Evaluation, or NURE, program of the Department of Energy and its predecessor, the Energy Research and Development Administration. The most useful feature of the program from the standpoint of indoor radon was the National Airborne Radiometric Reconnaissance, a set of airplane and helicopter flights along which the gamma radiations from several natural radionuclides were recorded. One of the radiations was from the bluish-214 decay product of radon, and is a reasonable measure of the mobile-plus-immobile radon in the top 25 cm of the ground. Although the NURE survey quadrangles cover nearly all the conterminous 48 states and half of Alaska, the actual ground coverage is

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used at some remedial action areas is reached without radium enrichment of the soil. To what extent radon can be drawn into a structure depends in part on the ease with which it can move from the site of its origin to the structure.

Radon Migration in the Ground. In comparison with radon in the air, radon in the ground is a gas of a given amount decaying in 3.8 days to a 90 percent decay in 13 days. It does not combine with anything and is free to move in the ground if it can first get into the non-solid spaces in rock or soil. The "pores". Of the radon that is produced by radium decay, the fraction that gets into the pores was termed the emanating power by Rutherford in 1901, but in the 1960's various investigators started using a variety of terms for the same thing: emanation coefficient, emanating fraction, escape-to-production ratio, release ratio, and others. The emanating power of rocks and soils is determined mainly by what happens during the recoil of the radon atom that is formed when a radium atom disintegrates. Figure 3 is a schematic diagram that shows the possible endpoints after the kinetic energy of the recoiling radon ion has been spent. In compact granular material whose pores are filled with gas, nearly all recoiling ions either fail to escape the grains in which they originate or become lodged in adjacent grains. Those that lodge in adjacent grains do have some chance of escaping back into pores during a brief period during which the matter along their paths is gaseous because of the great amount of energy released. Most of the atoms are trapped. However, a film of lipid of about 0.1- μ m thickness absorbs the recoil energy of the radon ion and stops it in the pore, so that it is then free to move. In this way, a small amount of capillary water raises the emanating power of granular material from the one or two per cent characteristic of desiccated material to the (35,20%) that is typical of soils.

Once the radon is in pores, moisture hinders its further movement. The principal mechanism of radon movement in pores typical of earth materials are molecular diffusion, with which no net movement of the major fluids are carried along with major fluids, such as soil air or water. The distance that radon can move by diffusion before 90% decays ranges from about 5 cm in gravel to about 2 cm in saturated sand or clay; diffusive movement greater than one meter is probably unusual. When a pressure difference pushes air through the soil and carries radon with it, the convective component of radon movement can exceed the diffusive component. The permeability of the ground is the measure of the ease with which soil air can be driven through it. Both diffusivity and permeability are greatest for dry, coarse material and least for water-saturated, fine-grained material, but permeability ranges over substantially wider limits. Significant convective flow of radon-bearing ground air is conceivable for distances of hundreds of meters in open fracture systems in rock, but is unlikely to approach such distances in soils. I estimate that radon movement by diffusion and convection combined is usually less than two or three meters. This estimate is consistent with the results of some careful measurements of radon and other relevant quantities in a gravely sandy loam in a semi-arid environment.

Classification of the Radon Potential of Areas

The inherent ability of the ground to supply radon to structures built on it is really the characteristic that we need to advise us to what extent structures in a locality are in need of extensive indoor radon testing or to advise us of the radon potential of localities not having enough structures to constitute an adequate sampling population. Lacking an established term I am calling this characteristic the radon availability of a site. I am not aware of work done to define either the dimensions or range of the quan-

not so good. Many of the survey quadrangles were flown at a flight line spacing of 5 miles. Because the width of the track along which information was obtained is only about 1600 ft, a survey at such spacing yields only about 5% coverage. The MURE data are consequently useful to detect regional trends, long features, and features that fortuitously lie on the flight paths, but they do not generally facilitate detection of hot spots. Coupled with information from geologic mapping they can, however, be quite useful. Another problem with the MURE data is that they are inconsistent. Although the contractors' systems were calibrated at the same site, results at the boundaries of two quadrangles may differ by a factor of two, and inconsistencies are sometimes seen even within the same quadrangle. One must check the data carefully before using them. The MURE "uranium anomaly maps", although they might show very local hot spots, have little use for predicting radon potential of areas.

In order to obtain the best from the MURE data, a method has been developed within the U. S. Geological Survey that facilitates comparison of the various radionuclide data. The entire range of the data for the set for each nuclide is digitized into 256 channels. For each of three parameters (radionuclide counting rate or the ratio of one radionuclide counting rate to another), a film map is produced on which lightness is proportional to the channel number for each spot. The maps are colored red, green, and blue, respectively, and superposed. Places where all three of the plotted parameters are high appear on the composite map as bright spots. A composite map in which the three parameters are uranium, thorium, and potassium is useful to show areas of outcrop of rocks such as granite, where all three parameters are usually high and there has been little depletion of the radionuclides. Where uranium has undergone some sort of concentration relative to thorium and potassium, uranium is compared with the ratio of uranium to thorium and with the ratio of uranium to potassium. The resulting uranium composite has proved useful for finding uranium deposits and is being examined as a tool for locating indoor radon hot spots.

Indoor radon surveys have, in general, shown a fair correlation with radium concentration in the ground. The correlation is best where the indoor radon values are well above action levels and not so good where they are low and more strongly influenced by the construction from building materials. As a means of predicting the radon potential of radonologically high areas of considerable extent, the MURE data have utility. Nonradioactive data at much closer flight line spacing would have to be obtained in order to find hot spots systematically.

If the finding of very hot spots is of high priority, I suggest that a careful review of uranium exploration surveys and literature by people who know both uranium geology and radon behavior would be the most expeditious. As a result of the extensive uranium exploration activity of the past 40 years, we should expect that rather few near-surface strong enrichments of uranium-series activity are undiscovered in the lower 48 States. These hot spots are special situations, however, and are only part of the indoor radon problem. The more difficult part concerns areas where radium is not strongly enriched in the soil.

The distribution of many elements in nature is another example of the log-normal distribution, and radium is probably no exception. Most radium concentrations in soil are low and in the region of high probability, but unfortunately not so low that they can be dismissed as generators of radon levels of concern. Armed with a few well-established numbers, one can calculate that very average soil contains 10⁴ to 10⁵ picocuries of radon per liter of soil air. If enough soil air can be drawn into a structure to constitute several percent of the air in the structure, the 4 pCi/L criterion

city, but I anticipate that the quantity will be defined and the measurement protocol established within the next year. It is principally dependent upon (1) the concentration of radon in the soil air at the point from which it is drawn, (2) the rate of extraction of the soil air, and (3) the pressure difference needed to extract it. Just as indoor radon measurements themselves are affected by precipitation, snow cover, freezing of the ground, and barometric pressure variations, those meteorological factors can be expected to make radon availability somewhat variable, particularly as they affect the fractional water saturation of the pores and fractures. However, the radon entry pathways, heating of structures, and generation of pressure differences by wind, which have profound effects on indoor radon levels, should have no effect on the radon availability measurement. The measurement could be used at whatever depths were appropriate in layered and anisotropic soils. In addition to its being more efficient and independent of the extraneous influences of individual building characteristics, the radon availability measurement should largely avoid the practical problems of cooperation with homeowners and the need to safeguard the results of measurements made in their homes. The radon availability measurement could be used to classify land at a finer scale than the high, normal, or low classifications used in Sweden to characterize the indoor radon potential of areas.

The Swedish classification is done according to the geological characteristics of an area. Although nearly every indoor radon survey has noted some correlation between high indoor radon and the underlying soil, rock, or topographic characteristics, the scatter of the data has raised doubts about the accuracy of prediction based on geologic data. The scatter may be due to the building factors mentioned earlier and to inadequate knowledge of the permeability and related characteristics of the ground in the areas surveyed. Geologic formations and rock types are not classified on the basis of their permeability, nor is permeability usually the primary basis for soil classification. Estimation of radon availability at present must rely on knowledge of the typical associations among uranium-series radionuclides and the various rock and soil types, the typical effects of deformation and weathering of rock to make it more permeable and to produce soil, the effects of glaciation, and the ways in which topography affects groundwater movement and influences permeability. The principles are clear enough, but their application to prediction of radon availability is speculative at present.

Correlations Between Geologic Features and Indoor Radon

Some correlations have already been reported between geologic features and radon concentrations in buildings situated on them. Other correlations may be inferred on the basis of expectations about their radium concentrations and the factors that govern radon migration. Use of both the observed and the expected correlations is speculative to some degree, because even a specific rock type that has been implicated as a source of high indoor radon in one study may differ from other rocks of the same type in some critical characteristic, such as extensive fracturing.

The igneous rocks are derived from a molten mix of silicates, oxides, and minor or trace amounts of most of the elements, including the radioactive ones. As this mix cools, the major silicates of high melting point solidify. Uranium, in particular, is incompatible with the structure of the major silicates, and stays in the melt while silicates of progressively lower melting point solidify. The last part of the melt to solidify is usually of the composition that classifies it as a granite or granodiorite, and it is with these rocks that uranium and thorium are usually found in the greatest abundance. The Scandinavian granites have been found to correlate with excessive indoor radon levels, and in Sweden are a basis for classifying

an area as "high". In New England, many wells drilled into granite produce water that has a radon concentration high enough to raise indoor radon levels significantly.

As rocks are broken down by water, thermal expansion and contraction, wind, and earth movement, the products, ranging from large blocks to fine particles and solutions, may become the first stage of the formation of a sedimentary rock. Uranium tends to become oxidized and mobile by these "weathering" processes, whence it may move to the sea or may become immobilized again upon being reduced, usually as a result of organic activity. Subsequent compaction and cementation can produce a sedimentary rock that is enriched in uranium, and further heat, pressure, and time can convert the rock to various grades of metamorphic rocks. In the last, greater radioactivity has been found to be associated with the earlier stages of metamorphism, but in the East, some of the rocks of the greatest uranium-series radioactivity are late-stage, high-grade metamorphic rocks called gneisses. The Reading Prong of Pennsylvania, New Jersey, and New York is a heterogeneous province of nonuniform radioactivity. At least some of its radioactive units are old gneisses probably derived from sediments that were enriched in uranium. Later periods of mountain building and deformation have altered and fractured the gneisses, so that they have increased permeability, as well as an enrichment of uranium-series radionuclides. Other deformed gneisses are present in the Appalachians, and need to be investigated with respect to their radon potential. Gneisses are found elsewhere in the U. S., but are generally younger and less deformed; their potential for very high radon availability is unknown.

Great biological activity in shallow seas can produce a reducing environment to cause precipitation of uranium from water. The product is somewhat a dark shale of elevated uranium-series radioactivity. An example, the Swedish "alum shale", has produced high indoor radon levels in houses built on it as an aggregate. In the United States, extensive areas of dark shales of lower radioactivity than the Swedish alum shale, are found to the north and west of the Appalachians. One of the dark shales in New York State has been found to correlate with higher indoor radon levels than do the regional sandstone formations.

In the marine environment, uranium often is adsorbed or precipitated with phosphate. Structures built on soil overlying near-surface phosphate beds, on the material remaining after extraction of phosphate, or on soil heavily treated with partially refined phosphate fertilizers may have elevated levels of indoor radon.

Limestones and dolomites are usually considered to be among the least radioactive rocks on a basis of their bulk radioactivity. However, they are susceptible to recrystallization, which produces rocks consisting of fairly pure calcium or calcium-magnesium carbonate crystals plus intergranular refuse of all the other elements that were present in the original sediments. In dolomites these intergranular spaces can be quite large and interconnected. Uranium-series radioactivity is concentrated in the spaces, where it is available to fluids moving through the rock. Higher indoor radon levels have been reported in houses located on a porous dolomite ridge around Oak Ridge, Tennessee, than in the valley below.

Limestones may be dissolved slowly by water, leaving a reddish-brown soil known as a *laterite*. The distinctive color is caused by oxidation of iron, which effectively scavenges radionuclides. Such residual soils may be sources of elevated indoor radon.

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Basal rocks that are of above-average uranium-series radioactivity and soils that are derived from them, some soils are good radon sources simply because they are very permeable. Gravel and sand of roughly uniform grain size are very permeable and drain well if there is some place for water to go. One very general effect of topographic relief is that the erosion of ridges and hillsides tends to carry the coarsest material the shortest distance and the finest material the greatest distance. The soil on the hillside is the coarsest material, and is well drained, so that it should have much higher permeability than that of the more level land below. The tendency of uranium-series radionuclides to prefer the finer sediments should compensate to some extent. If the soil on a ridge or hillside is thin, and the bedrock has the characteristic of any of the rocks mentioned earlier, there is a chance of considerably enhanced radon availability.

Glaciation can result in deposits of gravel or coarse sand. Such deposits should have high permeability and consequent enhanced radon availability. In addition, many of the glaciated areas in New England have bedrock of greater than average uranium-series radioactivity. In Scandinavia, long, sinuous ridges of stratified gravel and sand, associated with glaciation and known as eskers, are sources of elevated indoor radon levels. Other glacial deposits of gravel and sand, known as kames, appear as isolated or clustered mounds; they also are apt to have enhanced radon availability. Glacial till normally contains much fine sediment and is expected not to have enhanced radon availability unless the sediment is of unusually high radioactivity.

Clays and muds are composed of fine particles with small pores. They hold much capillary water, which tends to close inter-pore openings and to inhibit both diffusion and convective flow from pore to pore. Clays and muds normally retain water effectively, and if nearly saturated they should have low radon availability. If ground fails to pass the percolation test that is used to determine its suitability for a septic drain field, it should have low permeability and radon availability.

Clays and muds tend to crack if they are dried, however, which should lead to markedly increased permeability. The city of Winnipeg, Manitoba, has the highest average indoor radon levels found in the Canadian national survey¹⁵. The city is underlain by a thick clay layer that is dry and has extensive cracks¹⁶.

In the oxidizing surface environment, uranium is readily leached from many source rocks and may be adsorbed on soil particles in a "dispersion halo" covering a much larger area than that of the source rock. A dispersion halo occurs in the downward direction of surface and ground water movement, but because the halo may be the result of very long periods of dispersion (even millions of years), the direction of contemporary water movement may not be a reliable indicator of the location of an expected halo.

Some instances of high indoor radon arise from unusual circumstances. The first two of these special situations depend on close contact between structures and fractured rock of greater uranium-series radioactivity than the soil derived from it. Because of the tendency of radioactivity to be leached from soil and the lesser permeability expected for the soil, a few meters of soil should tend to insulate houses from radon issuing from uranium-enriched permeable rock. The striking house-to-house differences in indoor radon levels in one locality of the Reading Prong are probably due to this effect. Localities that have uranium enrichment in vein deposits, in shear zones, and in dikes of pegmatite (a coarse-grained rock usually of granitic composition) require close assessment to avoid mislabeled houses having severely elevated indoor radon levels.

The indoor radon problem associated with reclaimed phosphate land and radium-contaminated land, and technological enhancement, such as by use of uranium mill tailings for building foundations and concrete blocks, are obvious and well known.

As was mentioned above, wells drilled into fractured granite or gneiss sometimes yield water of very high radon content. Concentrations in excess of 10⁴ to 10⁵ pCi/L can result in significant indoor radon levels by the outgassing of radon from the water in showers, baths, laundries, and other domestic uses. Geologic regimes that are associated with such high concentrations of radon in water often have enhanced soil radon availability also.

Conclusions

In attempting to predict the indoor radon potential of areas, we are doubtful in for some unpleasant surprises. However, radon availability bears a sensible relationship to geologic factors. As our experience accumulates, we should become more competent and efficient in classifying indoor radon potential. On-site measurements of radon availability can be used to refine the estimates at a local scale, especially where the geology is heterogeneous or the topography is irregular.

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Figure 1. Log-normal probability frequency distribution. The theoretical distribution extends to infinity, but is bounded in practical applications.

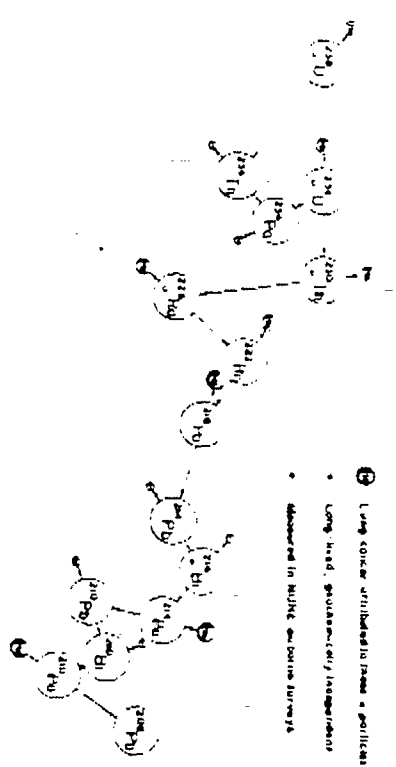


Figure 2. Uranium-238 series decay scheme. Some infrequent transitions have been omitted. Circles containing "He" denote alpha particles (helium nuclei). Circles containing "-" denote beta particles (electrons).

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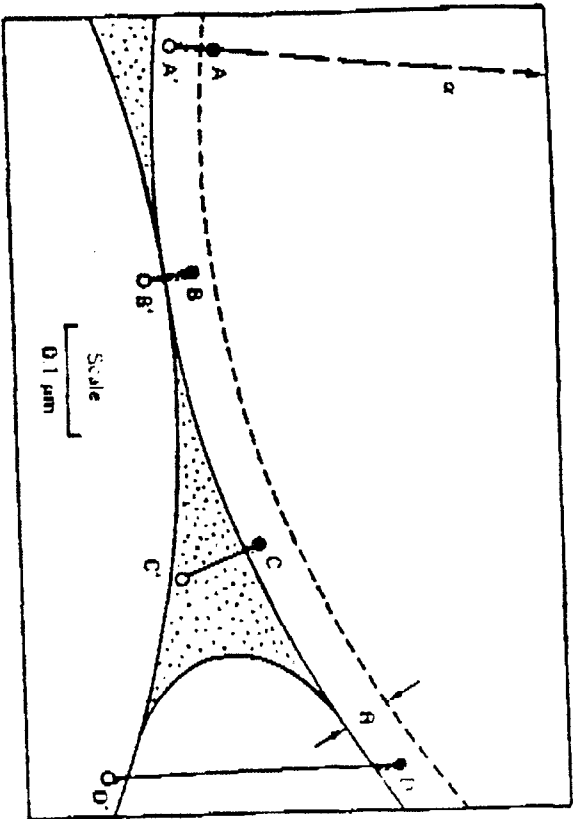


Figure 3.

Schematic diagram of the emanation process. The solid arcs represent the surfaces of two small spherical grains, about the size of clay particles. The recoil range, R , about 40 nm, is the distance between the dashed line and the surface of the upper grain. After the disintegration of radium atom A, the radon atom A' is stopped before it can reach the grain surface. Radium atom B' escapes from one grain only to be trapped in an adjacent one. Likewise radon atom D' traverses an air gap with little loss of energy and is trapped in the adjacent grain. Atom C' escapes from the first grain and loses any remaining kinetic energy in a water layer of 0.1 μ m.

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A few factors which govern the transport of radon from soil gas into a house are presented. Changing water vapor pressure in soil due to temperature pulses as well as barometric pressure can produce radon variations of events that are visible in the data. Soil temperature may affect the diffusion baseline. Indoor radon in this house consists of a baseline concentration due to diffusion with superimposed events occurring periodically. Diffusion contributed 60% of the soil related radon with 40% coming from events during the time period presented.

K. Rajagop
3/23/88



JACOBS ENGINEERING GROUP INC.
ENVIRONMENTAL SYSTEMS DIVISION

ORIGINAL
(RUC)

8207 MELROSE DR., SUITE 114
LENEXA, KS 66214
(913) 492-9218

info to (7) etard 0
Armael 0

March 11, 1988

Mr. Steven Kinser
U.S. Environmental Protection Agency
Region VII
Superfund Branch
726 Minnesota Avenue
Kansas City, Kansas 66101


Re: Potential Biotransformations of Chemical Compounds
Detected at the Byers Warehouse Site
Work Assignment No. 235

Dear Mr. Kinser:

Please find enclosed an assessment of the results of chemical analysis of water samples from the warehouse basement and Well No. 2, in regard to potential biotransformation processes.

Please contact Jill Biesma, or me at 913-492-9218 should you have any questions.

Sincerely,


Gary E. Parker
Region VII Manager

GEP/djd

Enclosure

cc: Raja Krishnamoorthy
Linda McGowan
Chris Williams
Valda Terauds
Pam McKee
Mark Doolan
Jill Biesma

AR300821

March 14, 1988

TO: Steven Kinser, U.S. EPA Primary Contact

THRU: Jill Biesma, Jacobs Engineering Group Inc.,
Kansas City, MO (Region VII)

Linda McGowan, Jacobs Engineering Group, Inc.
Denver, CO (Region VIII)

Chris Williams, Jacobs Engineering Group, Inc.
Denver, CO (Region VIII)

Valda Terauds, Jacobs Engineering Group, Inc.
Albuquerque, NM

FROM: Dr. Rajagopal Krishnamoorthy, Jacobs Engineering
Group Inc., Houston, TX (Region VI)

SUBJECT: Evaluation of Groundwater Chemical Analyses Data
with Emphasis on Potential Subsurface Contaminant
Degradation at the Byers Warehouse Site, St.
Joseph, MO. Work Assignment No. 235

I. OBJECTIVE OF STUDY

In their memo of January 6, 1988, Vulcan Chemicals reported that concentrations of several compounds detected in the sample taken from Well No. 2 appeared to be "radically disproportional to all of the previous analyses of the basement intrusion water". The objective of this study was to evaluate whether: (a) the basement water could have had an influence on the quality of the groundwater sample taken from Monitoring Well No. 2, and (b) such anomalies are possible if the degradation of chemical compounds in subsurface soils and aquifers is taken into consideration.

Limited site hydrogeologic information is presented below. This discussion is followed by a summary of potential biotransformation processes for each chemical compound detected in the groundwater sample from Well No. 2.

II. BACKGROUND

A. Site Hydrogeology (Refs. 1,2,3)

Very little site-specific hydrogeologic data is currently available. This information consists primarily of data collected during the installation of three groundwater monitoring wells at the site. According to the boring logs for these wells, the site is underlain by Holocene-age

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alluvium, which consists of clays, silts, sands, and some gravel. The depth to bedrock is estimated to be greater than 78 feet below the ground surface, as bedrock was not encountered during boring No. 1, which was completed to a depth of 78 feet. Other borings in the vicinity of the site indicate that bedrock may be encountered at approximately 100 feet below the ground surface. Bedrock in the region encompassing the site consists primarily of interbedded limestones and shales. These units range in thickness from less than a foot to approximately 20 feet, and are classified as belonging to the Lansing and Kansas City Groups, middle Pennsylvanian in age.

The unconsolidated deposits at the site appear to be heterogeneous, with the primary water-bearing units being silts, sands, and gravels interbedded within clay units. All three wells (1, 2, and 3) were completed in what appears to be clayey silts with a trace of sand and gravel. In each boring, groundwater was first encountered at approximately 15 feet below the ground surface. Due to the limited hydrogeologic data, the lateral and vertical continuity of the water-bearing units and potential contaminant pathways have not been defined.

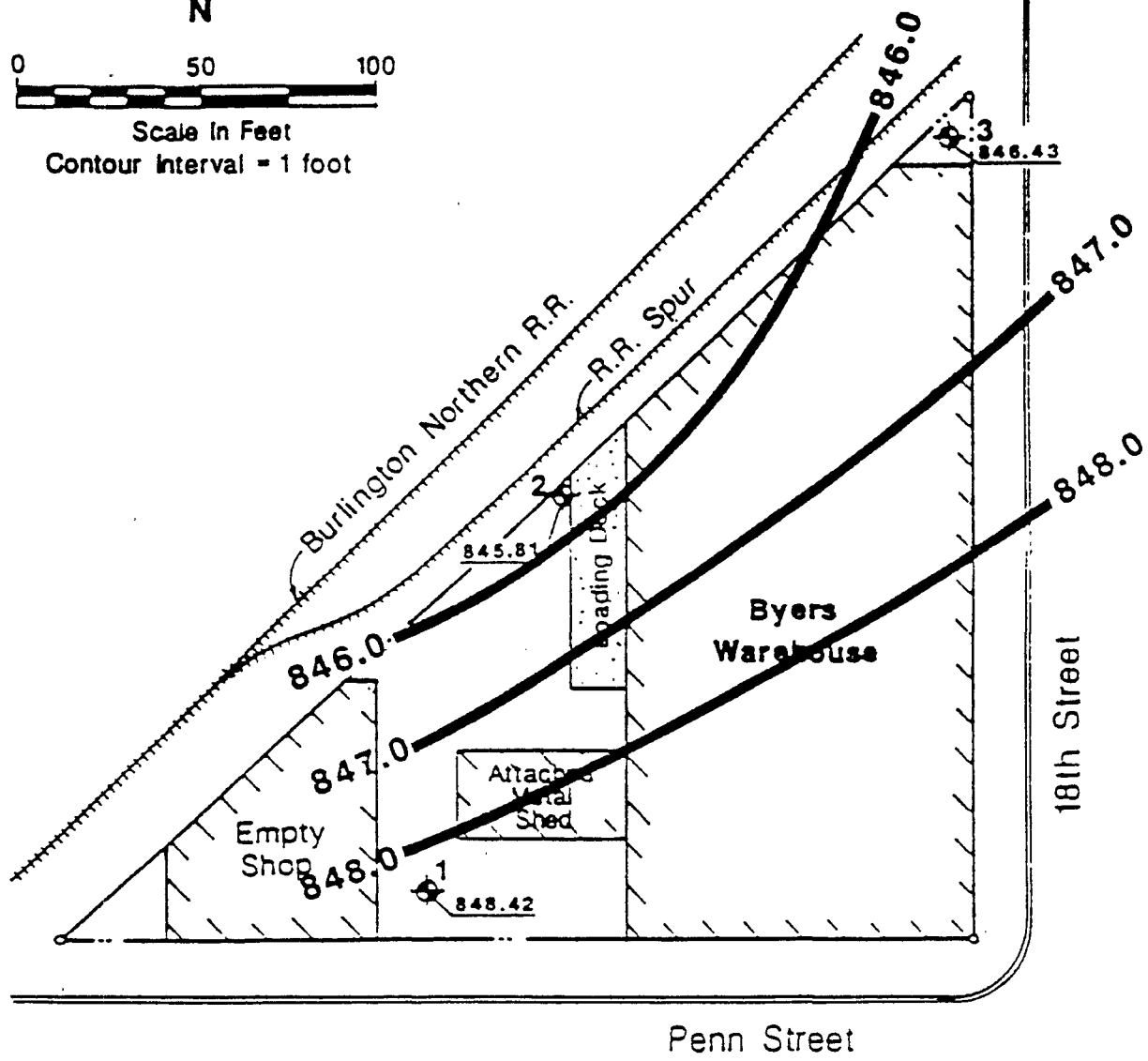
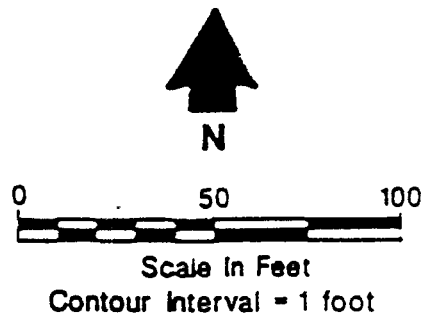
Vulcan's consultant has presented a potentiometric contour map of the unconfined alluvial aquifer, based on water level elevations in the three onsite wells on November 19, 1987. This map, included as Figure 1, shows the general direction of groundwater flow as toward the northwest. This figure also indicates that Well No. 2 is directly down-gradient from the warehouse basement, whereas Well No.1 and Well No.3 are cross-gradient.

It should be noted that three data points may not provide enough information to make a determination of the long-term flow pattern. There is a potential that localized sources of recharge (such as water lines, sewer lines) and drainage conduits (such as the 13-foot brick-lined combination sanitary-storm sewer adjacent to the site) may influence the groundwater flow pattern at the site. Without further data, potential contaminant pathways and groundwater velocities cannot be extrapolated. Investigations pertaining to the hydrogeologic conditions at the site are ongoing.

B. Site History (Refs. 2,4)

Byers Warehouse, located in a residential area in St. Joseph, Missouri, was used to store banned fumigants and pesticides. The building consists of two floors and a basement. The basement contained Ethylene Dibromide (EDB) in liquid formulations in 1 gallon, 5 gallon, and 55 gallon containers. Over time, some of these containers leaked. The basement floor has developed cracks and seepage of water into the basement has been observed. The water level in the

AR300823



LEGEND

○ Property Corner

1- Piezometer Location & Number

848.42 Elevation of Water (USGS Datum)

Figure 1.

PIEZOMETRIC CONTOUR MAP
BYERS WAREHOUSE

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PROJECT NO: 502.250

FIGURE NO.

DATE: November 24, 1987

2

basement has risen and fallen several times since the problem was discovered inadvertently by the local police.

The source of the basement intrusive water is not known at the present time. Possible sources under consideration include: (a) groundwater beneath the site, (b) water draining from the roof or from areas near the warehouse foundation during periods of precipitation, (c) a leaking water or sewer lateral near the warehouse basement, and (d) storm water flow in the combination storm and sanitary sewer adjacent to the site.

The top floor of the warehouse currently contains dry formulations of a Dimethylamine salt mixture containing 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) and 2,4-Dichlorophenoxyacetic Acid (2,4-D), while the ground floor contains both liquid and dry formulations of the same compound.

III. EVALUATION OF THE RESULTS OF CHEMICAL ANALYSIS

The results of chemical analyses of groundwater samples collected on December 8, 1987 from Well (Piezometer) No. 2, and the results of chemical analyses of several standing water samples from the warehouse basement and boiler room (collected in August and September of 1986) are presented in Table 1 (Ref. 5). The possibility of the occurrence of contaminants in Well No. 2 as a result of leakage of the chemicals in the warehouse basement is discussed in the following paragraphs.

A. Hydrogeological Data Related to Potential Contaminant Migration

Well No. 2, which appears to be down gradient from the warehouse basement, is located approximately 65 feet from the northwest corner of the boiler room (Figure 2). The first water strike in Well No. 2 occurred at approximately 14 to 15 feet below the ground surface. The well was screened from about 15 to 25 feet below the ground surface. The depth to water in the well was approximately 9.6 feet below the ground surface on November 19, 1987 (Ref. 1). The basement is estimated to extend about six to eight feet below the ground surface. Thus, it is possible that the basement floor is quite close to the water table in the shallow alluvial aquifer. The existing data is not sufficient for evaluating temporal variations in water levels in the shallow alluvial aquifer at the site. However, the possibility exists that high water table levels during periods of heavy precipitation may, in fact, intersect the basement. The possibility also exists that the basement intrusion water may leach from the basement into the vadose zone and then into the groundwater.

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TABLE 1. SAMPLE DATA-CONTAMINANT CONCENTRATIONS (ug/l)

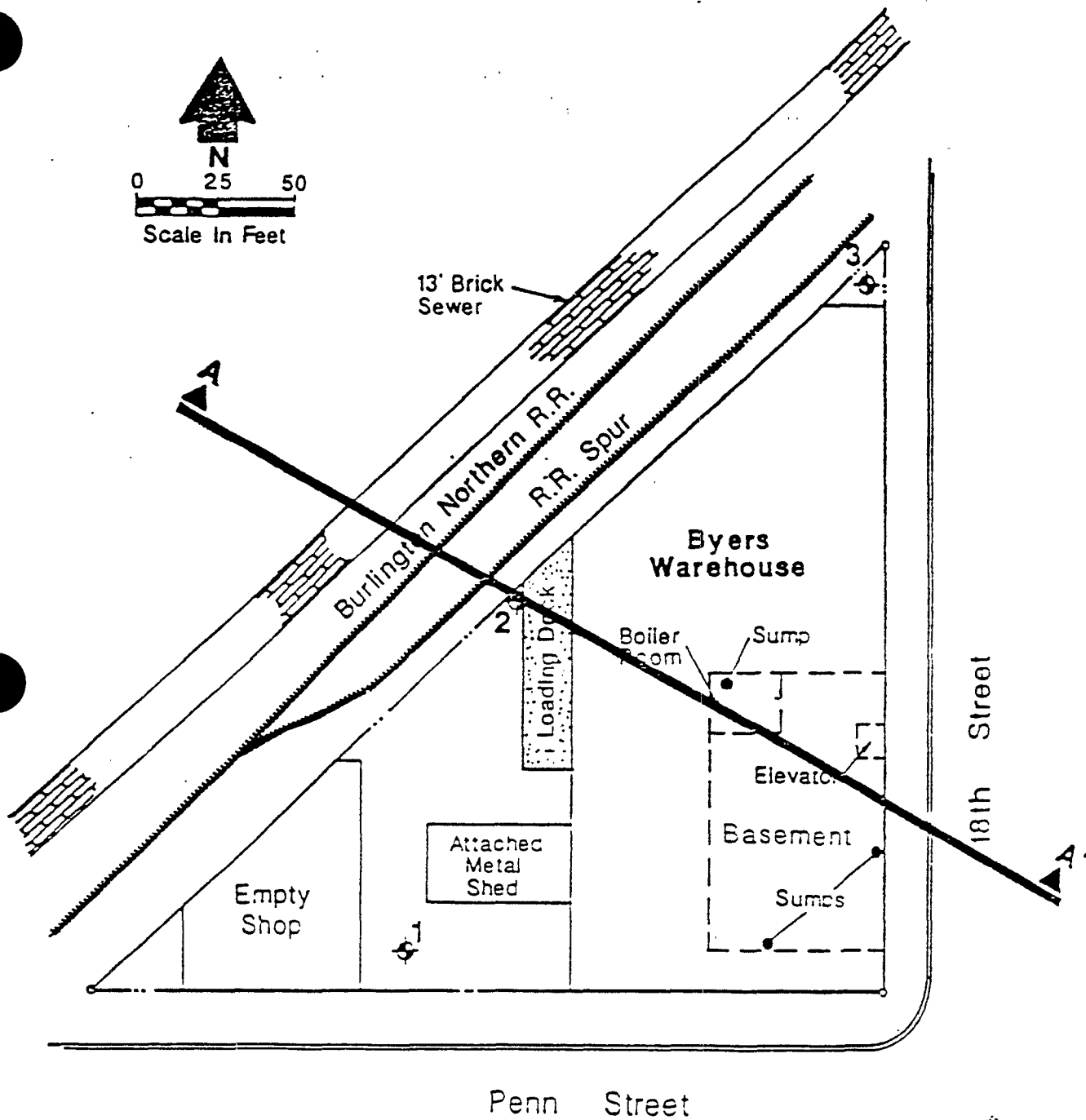
CONTAMINANT	EPA SAMPLE AAC61012 18TH & SPRING 8/15/86	EPA SAMPLE AAC61013 SUMP E. WALL 8/15/86	EPA SAMPLE AAC61014 SUMP SW CORNER 8/15/86	EPA SAMPLE AAC61015 SUMP NW CORNER 8/15/86	EPA SAMPLE AAC61021 BASEMENT 8/20/86	EPA SAMPLE AAC61033 BOILER ROOM 9/20/86	EPA SAMPLE AAC61034 BASEMENT 9/23/86	EPA SAMPLE AAC61035 BASEMENT 9/23/86	VULCAN CHEMICAL WELL#2 12/9/87
1,1,2,2-TETRACHLOROETHANE	ND (1.0)	3	2	3	ND (1.0)	2.4	ND (1.0)	ND (1.0)	8.3
CHLOROFORM	70	91	79	66	8100	28000	690	830	330
CARBON TETRACHLORIDE	83	ND (1.0)	280	290	44000	25000	23000	24000	ND (5.0)
TRICHLOROETHYLENE (TCE)	ND (1.0)	36	27	32	ND (1.0)	16	ND (1.0)	ND (1.0)	41
ETHYLENE DIBROMIDE (EDB)	110	170L	170L	170L	21000	170000	1300	3200	30
ETHYLENE DICHLORIDE (EDC)	710	53	270	72	14000	ND (1.0)	5100	5200	810
1,1,2,2-TETRACHLOROETHYLENE	ND (1.0)	68	38	70	ND (1.0)	43	5	2	740
1,2 DICHLOROPROPANE	6	ND (1.0)	ND (1.0)	ND (1.0)	250	2400	35	ND (1.0)	ND (5.0)
CARBON DISULFIDE	ND (5.0)	ND (1.0)	75	21	NA	NA	NA	NA	NA
CHLOROMETHANE	ND (12.0)	750	730	920	ND (12.0)	420	ND (12.0)	ND (12.0)	NA
VINYL CHLORIDE	ND (14.0)	5200	3300	3800	ND (14.0)	600	ND (14.0)	ND (14.0)	ND (5.0)
1,1-DICHLOROETHYLENE	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	35
METHYLENE CHLORIDE	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)	6.1
1,1,1-TRICHLOROETHANE	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	36
BROMOMETHANE	ND (12.0)	ND (12.0)	ND (12.0)	ND (12.0)	ND (12.0)	370	ND (12.0)	ND (12.0)	NA

1.-Concentration is known to be
higher than value reported

NA=Sample not analyzed for this
contaminant

References:
Report for Byers Commercial Warehouse, St. Joseph, Missouri, Roy F. Weston,
December 31, 1986, Appendix 1.
Correspondence from Steve J. Holly, Vulcan Chemicals, to Steve Kinser,
U.S. Environmental Protection Agency, January 6, 1988.

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LEGEND

- Property Corner
- ⊕ 1 Piezometer/Well Location & Number
- A—A' Cross Section

Figure 2.

CROSS SECTION LOCATION MAP
Byers Warehouse

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PROJECT NO: 502.250

FIGURE NO

DATE: February 4, 1988

B. Other Factors Influencing Contaminant Transport

The transport of organic contaminants in groundwater is affected by several factors in addition to groundwater gradients and hydraulic conductivities of subsurface soils. Transport of dissolved organic contaminants can be influenced by advection, dispersion, sorption and retardation, and chemical and biological transformations (Ref. 21). Factors affecting the transport of immiscible organic liquid phases include density and viscosity (Ref. 21). Thus, contaminant transport at a specific site is highly dependent on the physical and chemical properties of the contaminants in addition to the site environmental conditions.

Additional data are required to assess the transport rates and environmental fate of contaminants at the Byers Warehouse site. However, microbial activity is believed to be responsible for a portion of the observed differences in contaminant concentrations associated with the groundwater sample from Well No. 2 and the basement water samples.

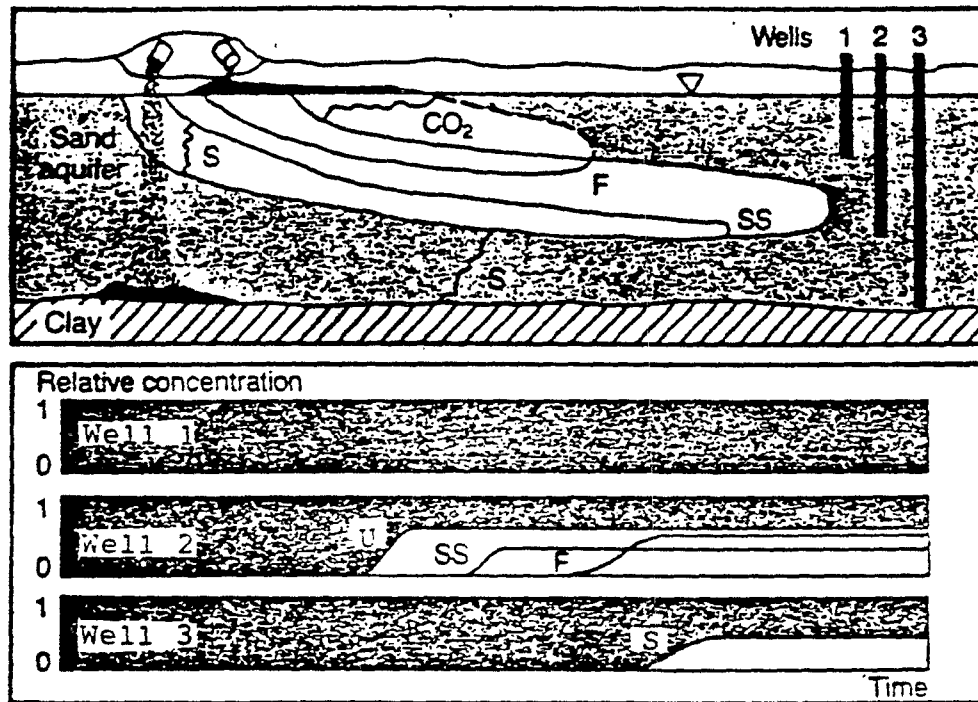
Transformations mediated by microorganisms are generally rapid compared to most chemical reactions occurring in shallow water table aquifers (Ref. 21). Many factors affect the rates of biotransformation of organic compounds, including water temperature and pH, the number and species of microorganisms present, the concentration of the substrata, the presence of microbial toxicants and nutrients, and the availability of electron acceptors (Ref. 21). Many shallow water table aquifers contain at least 10^6 microorganisms per gram of aquifer material (Ref. 7) and surprisingly high numbers of bacteria have been found in shallow, unconfined aquifers at depths of six meters or less (Ref. 21). Thus, it is quite possible that conditions suitable for biotransformation exist in the shallow alluvial aquifer below the site.

C. Example of Potential Chemical Biotransformations in an Aquifer Environment

The following paragraph presents the potential fate of several organic contaminants with different potentials for biotransformation in a hypothetical environment. This scenario involves a bulk waste which releases a continuous source of dissolved and unretarded solutes (U), and two pulse sources (F and S) in a very simple hydrogeologic domain: a uniform, unconfined sandy aquifer underlain by a horizontal aquitard. One of the two pulse sources has a specific gravity greater than one (S for sinker) and the other has a specific gravity less than one (F for floater). This hypothetical case is shown on Figure 3 (Ref. 21).

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Figure 3.



Continuous source of dissolved, unretarded solutes (U) and two pulse sources: floater (F) and sinker (S). The aquifer is aerobic except within the anaerobic U plume. Dissolved F degrades aerobically to CO₂ and water. Dissolved S degrades anaerobically to by-product SS, which is not readily degraded and is less retarded than S or F (Ref. 21).

Assume the leachate from the bulk waste contains readily biodegradable organic solutes. Assume also that the resultant microbiological growth in the aquifer renders the traversed zone anaerobic, as shown by the nonsorbing tracer U on Figure 3. The remainder of the saturated zone stays aerobic. A small source releases an organic liquid "floater" F, which is slightly soluble. Once contaminant F is dissolved, it can be completely mineralized (transformed to CO₂) under aerobic conditions, but it is not biotransformable under anaerobic conditions. Another small source releases an organic liquid "sinker" S, which is slightly soluble. The dissolved contaminant S is not transformable aerobically, but can be biotransformed under anaerobic conditions to an intermediate SS, which is more mobile than S and not readily degradable. In this case, contaminant F disappears from the aerobic zone above the leachate plume but persists within the plume. Conversely, contaminant S persists below the bulk leachate plume but disappears within the plume. Contaminant SS, which would not be found in the waste source itself, appears within the bulk waste leachate plume as a result of biotransformation. In this simplified portrayal, no contaminants are observed in Well No. 1 as shown on Figure 3. Well No. 2, however, is affected by the bulk leachate plume U, the persistent portion of the F plume, and the transformation product SS. Well No. 3 is affected by contaminant S only.

The above discussion suggests that, (a) both aerobic and anaerobic transformations of organic contaminants in shallow, unconfined aquifers can occur given the proper environmental conditions, and (b) depending on site-specific conditions, anomalies can be observed between the concentrations of contaminants at the source and in a monitoring well.

D. Potential Biotransformations of Chemical Compounds Detected at the Byers Warehouse Site

The apparent disproportionalities observed for specific compounds in Table 1 are evaluated in the following paragraphs in terms of potential microbial transformations in the shallow water table aquifer. Although other factors such as chemical reactions and volatilization of the contaminants could also play a role in the fate of the site contaminants, these factors are not discussed in detail in this report.

Specific data and information from selected research literature are presented with each chemical compound discussion, supporting the view that these processes may be occurring at the site. Much of the referenced material represents controlled laboratory experiments which may or may not be similar to the field conditions. At this time, the conditions of the aquifer relevant to biotransformation

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are not known. Therefore, while this report provides data supporting the hypothesis that these processes may be occurring at the site, the likelihood of the occurrence of these processes and the associated rates of transformation cannot be determined from the limited site-specific data.

More detailed information on biotransformations of these compounds is presented in the Appendix.

- (i) Ethylene Dibromide (EDB): The range of EDB concentrations found in the basement samples (including the boiler room) was 170 to 170,000 ppb and the concentration in Well No. 2 was 30 ppb. Research has shown that EDB degrades both aerobically and anaerobically in aquifer material (Appendix). Under experimental methanogenic conditions, greater than 99 percent of the EDB was removed in about four months. Under aerobic conditions, 10 to 12 percent of the initial EDB concentration was mineralized in five days. Downward migration of EDB (sp.gr.=2.17 at 20°C; water solubility =4000 mg/l at 20°C, pH 7) along with partial degradation by microorganisms could have resulted in the low detected concentrations of EDB in Well No. 2. Intermediate compounds were not observed, possibly due to complete mineralization of the biodegraded fraction by bacteria.
- (ii) 1,1,2,2-Tetrachloroethene (PCE): The range of PCE concentrations found in the basement samples was "not detected" (ND) (detection limit=1 ppb) to 70 ppb. The concentration in Well No. 2 was 740 ppb. Undissolved fractions of PCE (sp.gr.=1.63 at 20°C; water solubility=200 mg/l) could have migrated downward to the bottom of the aquifer. A portion could have dissolved in the water table and been detected in Well No. 2. It is possible that the original concentration of PCE in the basement before its discovery was greater than 70 ppb. Research has shown that under anaerobic conditions, PCE can degrade to trichloroethene (TCE) in aquifer materials (Appendix). In laboratory experiments initial ppm levels of PCE were biotransformed to ppb levels of TCE in about two months. Only a small fraction of PCE undergoes transformation (reductive dechlorination). This could have occurred in the aquifer at the site, resulting in the detected 41 ppb of trichloroethene in Well No. 2. The intermediates of PCE degradation, 1,2-dichloroethene (1,2-DCE) and vinyl chloride (VC) were not detected in Well No. 2, possibly due to further degradation to harmless products (Appendix).

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- (iii) Carbon Tetrachloride (CT): The concentrations of CT in the basement samples and Well No. 2 were ND(1.0 ppb) to 44,000 ppb and ND(5.0 ppb), respectively. Studies have shown that CT can be biodegraded under both methanogenic and denitrification conditions (Appendix). Both reductive dechlorination to yield chloroform(CF) and hydrolysis to yield carbon dioxide can occur. In laboratory experiments, nearly complete transformations of CT were reported to have occurred in three weeks to two months (Appendix). Thus, complete transformation of CT may have occurred in the site aquifer, leading to undetected levels of CT in Well No. 2. The formation of chloroform from CT might partially explain the detection of 350 ppb of chloroform in Well No. 2. It has been observed that less than 10 percent of CT is converted to chloroform in reductive dehalogenation (Appendix). A portion of CT could possibly have settled to the bottom of the site aquifer(sp.gr.=1.59 @ 20°C; water solubility=800 mg/l @ 20°C, pH 7). The transport of CT through the site soil materials could also have been retarded due to its high octanol-water partition coefficient (log Kow = 2.64).
- (iv) Chloroform (CF): The concentrations of chloroform observed in the basement water and Well No. 2 were 66 to 28,000 ppb and 350 ppb, respectively. Studies have shown that chloroform can be degraded anaerobically by methanogenic bacteria, but not by aerobic and denitrification bacteria (Appendix). In laboratory studies in the presence of methanogenic bacteria, CF was nearly completely transformed to carbon dioxide in 16 weeks, based on an initial concentration of 34 ppb, and 70 percent transformed in 16 weeks, based on an initial concentration of 157 ppb. In another study under acclimated methanogenic conditions, CF was nearly completely transformed to carbon dioxide after three weeks of incubation. In this study, the initial concentration of CF was less than 100 ppb (Appendix). Degradation of CF could have occurred in the site aquifer, resulting in detection of a low level of CF in Well No. 2. Methylene chloride, a structural analogue of the CF, can be removed in an anaerobic environment. As in the case of CT, a portion of the CF could also have settled to the bottom of the site aquifer (sp.gr.=1.48 @ 20°C; water solubility=8200 mg/l @ 20°C, pH 7). CF is the breakdown product of CT as described above.
- (v) Ethylene Dichloride (EDC): EDC concentration of ND(1.0 ppb) to 14,000 ppb and 810 ppb were observed in the basement water and Well No. 2, respectively. It has been suggested that EDC can degrade both aerobically

and anaerobically in groundwater. In laboratory experiments, the primary transformation product was carbon dioxide (Appendix). Under experimental methanogenic conditions, a concentration reduction of 63 percent was observed after about six months of incubation. Degradation of EDC could have occurred in the site aquifer, contributing to the low level detected in Well No. 2. Any undissolved portion of the EDC could have also settled to the bottom of the aquifer (sp.gr.=1.26 at 20°C; water solubility=8300 mg/l at 20°C, pH 7).

(vi) Trichloroethene(TCE): The concentrations of TCE in the basement water and Well No. 2 were ND(1.0 ppb) to 36 ppb and 41 ppb, respectively. TCE is an intermediate during the degradation of PCE(Appendix) and hence PCE degradation (a contaminant in the basement water in addition to Well No. 2) could have contributed to the detection of TCE in Well No. 2. Under anaerobic conditions, initial ppm levels of PCE have been shown to degrade by reductive dechlorination to ppb levels of TCE in about two months (Appendix). During a time span of about one and a half years, it is possible that 740 ppb of PCE in Well No. 2 could have yielded 41 ppb of TCE. It has been shown that reductive dechlorination of TCE is isomer specific and produces 1,2-DCE, not 1,1-DCE under anaerobic conditions (Appendix). It has also been shown that under methanogenic conditions, TCE can degrade slowly from an initial concentration of 155 ppb to as low as less than one ppb in about 10 months. TCE is not normally degraded under aerobic conditions. TCE is generally immiscible with and more dense than groundwater (sp.gr.=1.46 at 20°C; water solubility=1000 mg/l at 20°C, pH 7; log Kow=2.38). Thus, a portion of the TCE could have settled to the bottom of the aquifer, and contributed to the concentration observed in Well No. 2.

(vii) Methylene chloride(MC): The concentrations of methylene chloride in the basement water and Well No. 2 were ND(10 ppb) and 6.1 ppb, respectively. Although this compound was "undetected" in the basement water and detected in Well No. 2, it should be noted that the detection limit for the basement water was 10.0 ppb. Hence, methylene chloride could possibly have occurred in the basement water at a concentration below the detection limit. In general, MC is expected to degrade under aerobic conditions. In laboratory studies, MC has been shown to be degraded by methane-oxidizing bacteria and by Pseudomonas strains under oxygen-limiting conditions. MC is a structural analogue of CF and could be an intermediate formed during the anaerobic degradation of CF. MC is a dense, soluble

(polar) compound (sp.gr.=1.33 at 20°C; water solubility=20,000 mg/l at 25°C) Thus, MC can settle to the bottom of an aquifer or dissolve in water.

(viii) 1,1,2,2-Tetrachloroethane(1,1,2,2-TECA): The concentrations of 1,1,2,2-TECA in the basement water and Well No. 2 were ND(1.0 ppb) to 3 ppb and 8.3 ppb, respectively. Since 1,1,2,2-TECA is dense(sp.gr.=1.63 at 20°C) and not very soluble in water (water solubility=2,900 mg/l at 20°C, pH 7), it is possible that it could settle to the bottom of the aquifer. Its transport could have also been retarded by sorption onto soils (log Kow=2.56). It has also been shown that 1,1,2,2-TECA can be transformed to 1,1,2-Trichloroethane (1,1,2-TCA) under methanogenic conditions (Appendix). These factors could have contributed to the disproportionality observed in the chemical analyses.

(ix) 1,1,1-Trichloroethane(TCA): The concentrations of TCA in the basement water and Well No. 2 were ND(1.0 ppb) and 36 ppb, respectively. TCA is not expected to degrade aerobically or under denitrification conditions in groundwater(Appendix). It can be degraded to 1,1-DCA under anaerobic conditions and to 1,1-DCE under abiotic conditions(Appendix). Since TCA is dense(sp.gr.=1.34 at 20°C) and not very soluble in water(water solubility=4,400 mg/l at 20°C, pH 7), it is possible that any TCA that might have originally been present in the basement water could have settled to the bottom of the aquifer. A portion could also have dissolved in the groundwater, leading to detectable concentrations of TCA in Well No. 2.

(x) 1,1-Dichloroethene(DCE): The concentrations of DCE in the basement water and Well No. 2 were ND(1.0 ppb) and 35 ppb, respectively. DCE is a breakdown product of TCA, which was detected in Well No. 2 at 36 ppb. It is possible that the source of DCE in Well No. 2 was the degradation of TCA. DCE is a dense contaminant(sp. gr.=1.22) which is immiscible in water(water solubility=400 ppb at 20°C and pH 7). Thus, this contaminant could have settled to the bottom of the aquifer. Under methanogenic conditions, DCE in aquifer material can be converted to vinyl chloride (Appendix). An initial DCE concentration of 124 ppb was shown to degrade in a laboratory experiment to 1 ppb in approximately ten months.

IV. SUMMARY

This study has shown that anomalies such as the results of chemical analyses at the Byers Warehouse site are possible if a contaminant migration pathway exists between two

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sampling locations and if biotransformation reactions have occurred. Based on the above discussions it is quite possible that a migration pathway exists between the warehouse basement and Well No. 2. Furthermore, the conditions in the shallow alluvial aquifer below the site could potentially be suitable for biotransformation processes to occur. Thus, biotransformation of the chemical compounds detected in the standing water from the Byers Warehouse is considered a potential factor in the observed contaminant concentrations in the groundwater sample from Well No. 2.

Potential transformation of the chemical compounds detected in the samples of standing water from the warehouse basement are summarized in Table 2.

While this study provides data supporting the hypothesis that contaminant migration and biotransformation processes may be occurring at the site, the likelihood of contaminant migration and biotransformation cannot be determined from the limited site-specific data.

The following activities are proposed for future investigations to provide additional data for evaluating the potential for biotransformation at the Byers Warehouse site:

- o Assess the types and lateral and vertical concentration distribution of microorganisms present, if any, in the subsurface soil and the shallow alluvial aquifer.
- o Assess the soil and groundwater of the shallow alluvial aquifer in terms of the temperature; pH and reductive potential(Eh); dissolved oxygen; electron acceptors such as nitrates, sulfates, carbonates; methane; sulfides; BOD; COD; TOC; and other nutrients. This assessment should include the lateral and vertical profiles of these parameters, if appropriate.
- o Assess the presence of transformation products and intermediates in soil and groundwater samples from the shallow alluvial aquifer.
- o Quantify the contaminants present in the groundwater at the bottom of the shallow alluvial aquifer.
- o Determine the elevation of the basement and boiler room floors relative to the water level in Well No. 2.
- o Assess the average hydraulic conductivity of the shallow alluvial aquifer at the site.

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Compound	Detected Concentration Range (ppb) in Basement and Boiler Room Standing Water (08/87 and 09/87)	Detected Concentration (ppb) in Groundwater from Monitoring Well No. 2 (12/08/87)	Potential Aerobic Biotransformations		Potential Anaerobic/Ablative Biotransformations			
			Process	Parent Compound	Product(s)	Process	Parent Compound	Product(s)
1,1,2,2-Tetra- chloroethane (PCE)	ND(1)-70	740	NA	NA	NA	Reductive Dechlorination (Methanogenic)	1,1,2,2-tetra- chloroethane	Trichloroethane 1,2-Dichloroethane Vinyl Chloride
Carbon Tetra- chloride (CI)	ND(1)-14,000	ND(5)	NA	NA	NA	Reductive Dehalogenation (Methanogenic, Sulfidification)	Carbon Tetrachloride	Chloroform Carbon Disulfide
Chloroform (CF)	46-78,000	350				Hydrolysis (Sulfidification)	Carbon Tetrachloride	Carbon Disulfide
			NA	NA	NA	Re-oxidation (Methanogenic)	Chloroform	Carbon Disulfide
						Reductive Dehalogenation	Carbon Tetrachloride	Chloroform
Ethylene Dichloride (EDC)	ND(1)-14,000	810	Microbial Oxidation	Ethylene Dichloride	Carbon Disulfide (eventually)	Re-oxidation (Methanogenic)	Ethylene Dichloride	Carbon Disulfide
Ethylene Dibromide (EDB)	170-170,000	30	Oxidation	Ethylene dibromide	Carbon Disulfide (eventually)	Methanogenic Conditions	Ethylene Dibromide	Bromoethanol Other Volatile End Product
1,1,2,2-Tetra- chloroethane (1,1,2,2-TECA)	ND(1)-5	6.5	NA	NA	NA	Appears to be Reductive Dechlorination (Methanogenic)	1,1,2,2-Tetrachloro- ethane	1,1,2-Trichloroethane
Methylene Chloride (MC)	ND(10)	6.1	Oxidation	Methylene Chloride	Carbon Disulfide (eventually)	Oxygen Limiting Conditions (Pseudomonas)	Methylene Chloride	Non-chloromethanol Formaldehyde Carbon Disulfide
1,1,1-Trichloro- ethane (TCA)	ND(1)	36	NA	NA	NA	Reductive Dechlor- ination and Ablative Transformation	1,1,1-Trichloroethane	1,1-Dichloroethane Chloroethane Ethanol Carbon Disulfide 1,1-Dichloroethane Vinyl Chloride
Trichloroethane (TCE)	ND(1)-16	41	NA	NA	NA	Reductive Dechlor- ination (Methanogenic)	1,1,2,2-tetrachloro- ethane	Trichloroethane
1,2-Dichloro- ethane (1,2-DCE)	ND(1)	35					Trichloroethane	1,2-Dichloroethane Vinyl Chloride
			NA	NA	NA	Reductive Dechlor- ination (Methanogenic)	1,1-Dichloroethane	Vinyl Chloride
						Reductive Dechlor- ination and/or Ablative Transformation	1,1,1-Trichloroethane	1,1-Dichloroethane

Not Available

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APPENDIX

SELECTED TRANSFORMATION REACTIONS
FOR HALOGENATED ALIPHATIC COMPOUNDS
FOUND AT THE BYERS WAREHOUSE SITE

AR300839

TERMINOLOGY

COMETABOLISM: Refers to a microbiologically-induced change in a molecule that modifies the compound somewhat, but not to an extent sufficient for the responsible populations to utilize the substrate as a source of energy or of any nutrient element it contains. Hence, despite the alteration in the molecule, it is not mineralized, and products of the partial transformation accumulate in the environment.

Example: SUBSTRATE TRANSFORMATIONS BY BACTERIA

PRIMARY SUBSTRATES

AEROBIC & ANAEROBIC: GLUCOSE, ACETONE, ISOPROPANOL, ACETATE, BENZOATE, PHENOL

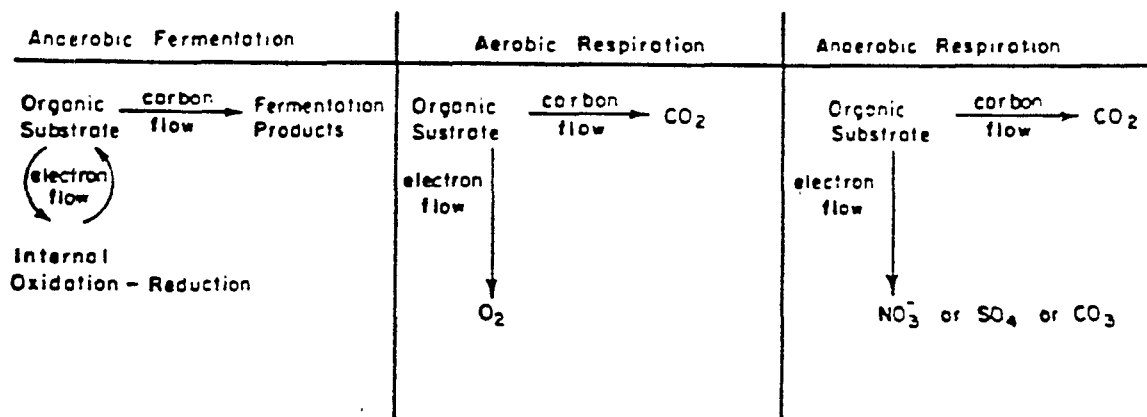
AEROBIC PRIMARILY: ALKANES, BENZENE, XYLENE, 1,2-DCA, CHLOROBENZENES, VINYL CHLORIDE

CO-METABOLISM

OXIDATIONS: TCE, DCE, VINYL CHLORIDE, 1,2-DCA, CHLOROFORM

REDUCTIONS: TCA, TCE, PCE, DCA, DCE, DDT, LINDANE, PCBS

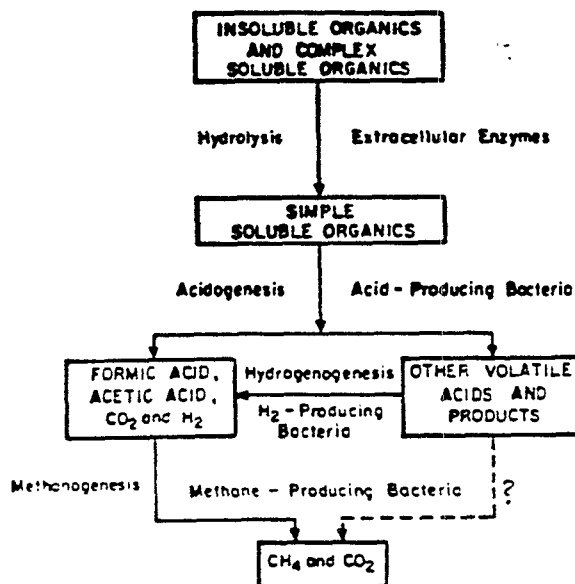
ANAEROBIC DEGRADATION OR FERMENTATION: Metabolism in the absence of oxygen. Occurs when the hydrogen acceptor is an organic compound which has been generated within the cell by metabolism of the original substrate. The general multistep nature of anaerobic processes is depicted below:



Multistep Nature of Anaerobic Operations.

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RESPIRATION: Respiration occurs when the hydrogen (electron) acceptor is an inorganic compound from the surrounding medium. Respiration may be further subdivided with respect to the inorganic acceptor molecule. If it is molecular oxygen, the respiration is referred to as aerobic. If it is some other inorganic ion, such as nitrate, sulfate or carbonate, the respiration is called anaerobic respiration. The following figure compares the basic features of fermentation and respiration.



Summary of Electron and Carbon Flow in Heterotrophic Metabolism

AEROBIC PROCESSES: Those biological processes that occur in the presence of oxygen (electron acceptor).

ANOXIC DENITRIFICATION: The process by which nitrate nitrogen (electron acceptor) is eventually converted biologically to nitrogen gas in the absence of nitrogen.

REDUCTIVE DEHALOGENATION: The biological replacement of a halogen with a hydrogen atom under anaerobic or anoxic conditions.

METHANE-UTILIZING BACTERIAL PROCESS: Process by which the growth and respiratory activity of methane-utilizing bacteria is enhanced under aerobic conditions with the addition of nutrients, such that they can metabolize synthetic organic chemicals (including halogenated compounds) either as primary or as secondary substrates.

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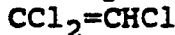
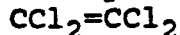
TRANSFORMATION REACTIONS

COMPOUND

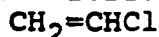
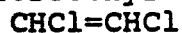
1,1,2,2-Tetrachloroethene(PCE) - Solvent, Perchloroethene

TRANSFORMATION REACTION/PRODUCTS

Tetrachloroethylene(PCE) ---> Trichloroethylene(TCE)



---> Dichloroethylenes(DCE) ---> Vinyl chloride(VC)



(Ref. 6,7,8,9)

---both cis- and trans- Dichloroethylene can be produced

(Ref. 8)

REMARKS

- o May be transformed under proper environmental conditions by microorganisms that are native to groundwater (Ref.6).
- o Process termed reductive dehalogenation, under anaerobic conditions, and where methane-forming bacteria are present and active(Ref. 6,7).
- o Parent and intermediate compounds frequently found in contaminated aquifers (Ref. 6,7).
- o In aquifers, half-lives for reductive dechlorination can be on the order of months to years (Ref. 6).
- o Products of reductive dechlorination are, in general more mobile.
- o Under appropriate conditions, vinyl chloride can be metabolized to harmless products (Ref. 7).
- o Reductive dechlorination of PCE and TCE in microcosms composed of aquifer materials produced both (cis- and trans-) isomers of 1,2-dichloroethene(DCE). Conditions were 25°C, dark environment, reductive environment (Eh=-60 to 60 mV) and neutral to acid pH(pH 5.0 to 7.2) (Ref. 8). An Eh lower than 350 mV is reported to be sufficiently reductive to effect significant dechlorination. The highest mineralization rates have been reported to occur at pH 8.0 and the lowest at pH 5.0 (Ref. 8).
- o Initial ppm levels of PCE or TCE resulted in ppb levels of TCE or DCE in seven to eight weeks, since only a small fraction of parent substrate undergoes reductive dechlorination (Ref. 8).
- o Tetrachloroethylene was biodegraded under laboratory conditions within about eight weeks undermethanogenic conditions (Initial concentration=200 ppb; 35°C and incubated in the dark) (Ref. 9).

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COMPOUND

Carbon Tetrachloride(CT) - Solvent, Tetrachloromethane

TRANSFORMATION REACTION/PRODUCTS

Reductive Dechlorination:

Carbon Tetrachloride(CT) ---> Chloroform(CF)
 CCl_4 CHCl_3

(Ref. 8, Ref. 10)

Hydrolysis:

Carbon Tetrachloride(CT) ---> Carbon Dioxide(CO_2)

(Ref. 9, Ref. 10)

REMARKS

- o The reactions were obtained in studies with aquifer material microcosms. Reductive dehalogenation was proposed as the transformation mechanism. Study conditions: 25°C, dark environment, absence of oxygen, neutral to acid pH, reductive potential(Ref. 8). Less than 10 percent of the CT added, appeared as chloroform. In two months, no trace of carbon tetrachloride was observed.
- o Under acclimated methanogenic laboratory conditions, CT was almost completely biooxidized to CO_2 . No chloroform was detected (Ref. 9). The range of concentrations used was about 10 to 30 micrograms per liter, and incubation was at 35°C in the dark. Nearly complete transformation of CT occurred after three weeks of incubation (Ref. 9).
- o Under anoxic, denitrification conditions in the laboratory, transformation of CT was observed after eight weeks in batch denitrification cultures. Both reductive dechlorination to chloroform and hydrolysis to CO_2 was observed (Ref. 10). Initial concentrations of CT were about 60 ppb. (Ref. 10).

COMPOUND

Chloroform(CF) - Solvent, Trichloromethane

TRANSFORMATION REACTION/PRODUCTS

Chloroform(CF) --> Carbon Dioxide(CO_2)
 CHCl_3

(Ref. 9)

AR300843

REMARKS

- o Aerobic microorganisms do not normally break down CF (Ref. 7,11).
- o Under acclimated methanogenic conditions in the laboratory, CF was nearly completely transformed to CO₂ after three weeks of incubation (Ref. 9). The initial concentration of CF was less than 100 ppb. The proposed mechanism was biooxidation.
- o CF at initial concentrations of 60 ppb (concentrations commonly found in groundwater) was not transformed under denitrification conditions in the laboratory (Ref. 10).
- o Chloroform degradation can occur anaerobically (Ref. 11). In the presence of methanogenic bacteria, chloroform was nearly completely transformed in 16 weeks at an initial concentration of 34 ppb and about 70 percent transformed in 16 weeks at an initial concentration of 157 ppb. Analyses were not made for intermediates. Preliminary evidence has indicated that methylene chloride, a structural analogue of chloroform, can be removed in an anaerobic environment. Absence of anaerobic conditions may explain why significant degradation of chloroform has not been observed during groundwater recharge (Ref. 11).

COMPOUND

Ethylene Dichloride (EDC) - 1,2-Dichloroethane, Ethylenechloride

TRANSFORMATION REACTION/PRODUCTS

Ethylene Dichloride (EDC) ---> expected to degrade aerobically
 $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$

(Ref. 7)

Ethylene Dichloride (EDC) ---> Carbon Dioxide (CO₂)
(methanogenic conditions)

(Ref. 9)

REMARKS

- o Of the chlorinated hydrocarbons commonly found in groundwater, a few compounds such as EDC (1,2-dichloroethane) can be expected to degrade in aerobic (oxygenated) groundwater (Ref. 7).
- o In a laboratory study under methanogenic conditions, 1,2-dichloroethane at initial concentrations of less than 100 ppb was found to be transformed. There was a

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concentration reduction of 63 percent after 25 weeks. No other haloorganic intermediates from the transformations could be detected by gas chromatography/mass spectrometry (GC/MS). The primary transformation product for 1,2-dichloroethane was CO_2 , probably the consequence of biological oxidations (Ref. 9).

COMPOUND

Ethylene Dibromide (EDB) - 1,2-Dibromoethane, Ethylenebromide

TRANSFORMATION REACTION/PRODUCTS

- (a) Ethylene Dibromide (EDB) ---> soluble intermediate
 $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$
---> Carbon Dioxide (CO_2) (by methane-oxidizing bacteria)
(Ref. 12)
- (b) Ethylene dibromide (EDB) ---> Carbon Dioxide (CO_2) (aerobic conditions)
(Ref. 13;15)
- (c) Ethylene dibromide (EDB) ---> degrades under methanogenic (anaerobic conditions)
(Ref. 14)

REMARKS

- o In a laboratory study under denitrification conditions, no indication of transformation of EDB was observed after eight weeks of incubation at an initial concentration of 60 ppb (concentration commonly found in groundwater) (Ref. 10). No significant degradation of EDB occurred.
- o EDB, a persistent chemical in the aquifer environment, can be degraded and mineralized by methane-oxidizing bacteria (Ref. 12). Mixed cultures of methanotrophs and soil microorganisms were used. EDB could be degraded at concentrations above one ppm. Methane is used as a sole carbon source.
- o Residual EDB in soil has been reported to be highly resistant to both mobilization and microbial degradation in contrast to freshly-added EDB. EDB is entrapped in intraparticle micropores. Release of residual EDB into aqueous solution was extremely slow at 25°C . Aerobic degradation of residual by indigenous microbes was negligible after 38 days compared to rapid removal of freshly-added EDB. This suggests that EDB is present at micropore sites that are sterically inaccessible to bacteria (Ref. 13).

- o Under methanogenic (anaerobic) conditions of incubation, the concentration of EDB in aquifer material tested in a laboratory decreased from 194 ppb to less than one ppb in 16 weeks (Ref. 14). Possible intermediates can be bromoethanol and a very volatile end product.
- o EDB-treated aquifer material showed mineralization without an acclimation period under aerobic conditions (Ref. 15). The EDB mineralized increased linearly to 10 to 12 percent of the initial concentration by day five and more slowly to 14 to 17 percent by day 11.

COMPOUND

1,1,2,2-Tetrachlorethane - (1,1,2,2-TECA)-Acetylene
Tetrachloride

TRANSFORMATION REACTION/PRODUCTS

1,1,2,2-Tetrachloroethane--->1,1,2-Trichloroethane
CHCl₂-CHCl₂ (1,1,2-TCA)
(methanogenic conditions)

(Ref. 9)

REMARKS

- o The initial step in the transformation of 1,1,2,2-tetrachloroethane to 1,1,2-TCA appeared to be by reductive dechlorination. The results were obtained under methanogenic conditions, in continuous fixed film columns in a laboratory study, with a two-day detention time. An influent concentration of 27±1 ppb was reduced to an effluent concentration of 0.90±0.7 ppb. (Ref. 9).

COMPOUND

Methylene Chloride(MC)-solvent, Dichloromethane,
Methylenedichloride

TRANSFORMATION REACTION/PRODUCTS

(a) Methylene Chloride--->expected to degrade aerobically
CH₂Cl₂

(Ref. 7).

(b) Methylene Chloride-->Formaldehyde-->Carbon Dioxide(CO₂)
(air-tight conditions)

(Ref. 16)

(c) Methylene Chloride--->can be degraded by methane
oxidizing bacteria

(Ref. 12)

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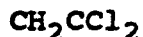
- o Trichloroethylene (TCE) was degraded from 477 ppb to nondetectable levels in incubated groundwater with methane-oxidizing bacteria, mineral nutrients, oxygen and methane (Ref. 12).
-

COMPOUND

1,1-Dichloroethene (1,1-DCE)-Solvent, 1,1-Dichloroethene, Vinylidene Chloride

TRANSFORMATION REACTION/PRODUCTS

- (a) 1,1-Dichloroethene (1,1-DCE) ---> see notes for TCA



(Refs. 6, 14, 17, 20)

REMARKS

- o Frequently found in groundwaters contaminated with PCE and TCE (Ref. 6).
 - o Studies with methane-utilizing bacteria have shown that DCE was degraded from an initial concentration of 630 ppb to 200 ppb in two to four days of incubation. No transformation products were produced under these conditions (i.e., vinyl chloride) (Ref. 19).
 - o Under anaerobic methanogenic studies in aquifer material, 1,1-DCE was converted to VC as the daughter product (Ref. 14). During 40 weeks of incubation, an initial concentration of 124 ppb of 1,1-DCE was degraded to less than one ppb.
 - o Vinyl chloride is produced by reductive dechlorination of 1,1-DCE. Other processes are possibly involved (Ref. 20). First order constants for depletion of parent materials ranged from 3.57×10^{-4} to 1.67×10^{-4} per hour.
-

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- o Under denitrification conditions, 1,1,1-TCA was not degraded after eight weeks of incubation. The initial concentration was 61 ppb (Ref. 10).
- o Relatively rapid transformation of TCA to 1,1-DCA (90 percent after six days detention in large anaerobic fixed film columns) occurred under biotic conditions. Under groundwater conditions, abiotic transformations (TCA to 1,1-DCE and TCA to acetic acid) might predominate in areas where little or no methanogenic activity occurs (Ref. 17).

COMPOUND

Trichloroethene(TCE)-Solvent, Ethylenetrichloride

TRANSFORMATION REACTION/PRODUCTS

- (a) Trichloroethene(TCE)--->see notes for PCE
 $\text{CCl}_2=\text{CHCl}$

(Refs. 6,7,14)

- (b) Trichloroethene(TCE)--->cis- and trans-1,2-
 Dichloroethene(1,2-DCE)
 $\text{CHCl}=\text{CHCl}$

(Ref. 8)

REMARKS

- o Aerobic microorganisms do not normally degrade TCE (Ref. 7,11).
- o In aquifer material microcosms studies in an oxygen-free environment, TCE was transformed to cis- and trans-1,2-DCE by reductive dechlorination. Initial concentrations of four to five mg/l produced as much as 167 ppb of 1,2-DCE after about eight weeks of incubation (Ref. 8).
- o Anaerobic degradation of TCE in soil produced only 1,2-DCE; no 1,1-DCE was observed (reductive dechlorination) (Ref.18). Concentrations of 2000 ppb of TCE produced 25 to 78 ppb of 1,2-DCE after about 10 months of incubation.
- o Low concentrations of TCE may not result in anaerobic degradation (Ref. 8).
- o Under conditions of methane-utilizing bacteria, TCE was degraded. Neither DCEs nor VC were produced. Only two to four days were required to degrade an initial concentration of 630 ng/ml to 200 ng/ml. (Ref. 19).
- o A laboratory study with methanogenic (anaerobic) aquifer material showed that TCE can be degraded from 155 ppb to less than one ppb in about 40 weeks (Ref.14).

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REMARKS

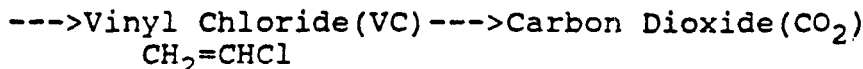
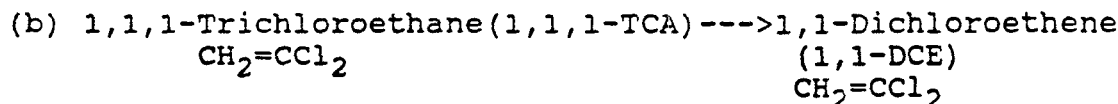
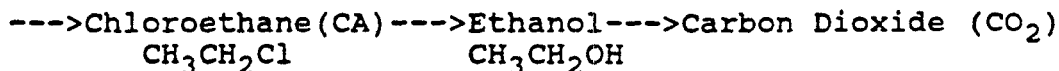
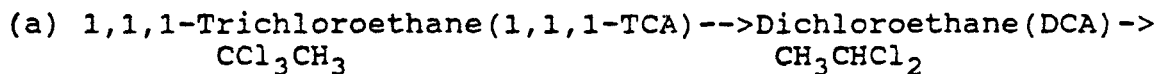
- o MC can be expected to degrade in oxygenated groundwater (aerobic conditions). (Ref. 7).
- o Under air-tight conditions, Pseudomonas strains growing on MC as the only carbon and energy source may convert MC to monochloromethanol, which spontaneously forms formaldehyde. Formaldehyde can be partially assimilated and partially oxidized to CO₂ (Ref. 16).
- o Under laboratory conditions, MC was degraded at concentrations above one ppm by methane-oxidizing bacteria (Ref. 12).
- o MC can be degraded in groundwater in the presence of methane-oxidizing bacteria, mineral nutrients, and oxygen. A decrease in MC from an initial concentration of 91 ppb to about 9 ppb occurred in less than two days (Ref. 12).

COMPOUND

1,1,1-Trichloroethane(1,1,1-TCA)-Solvent, Methylchloroform

TRANSFORMATION REACTION/PRODUCTS

Reductive Dechlorination and Abiotic Transformations:



(Ref. 6, 17)

REMARKS

- o Trichloroethane is not expected to be degraded by aerobic microorganisms (Ref. 7).
- o Under appropriate conditions, vinyl chloride can be metabolized to harmless products (such as CO₂) (Ref. 7).
- o In aquifer material microcosm studies, 1,1,1-TCA was shown to be converted to 1,1-DCA under anaerobic conditions (Ref. 8). Complete disappearance of 1,1,1-TCA occurred within four to five months. The observed pH range was 6.5 to 7.4 and the Eh range was -150 to 40 mV in seven to eight weeks (Ref. 8).

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